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Hydride Transfer Reactivity of $Mo(L)(H)(depe)_2$ (L = N, $NBEt_3$)

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Starting from $Mo(N_2)_2(depe)_2$ (**1**), the nitrido complex $Mo(N)(N_3)(depe)_2$ (**2**) was obtained by the reaction of **1** with Me_3SiN_3. Subsequent reaction of **2** with HCl in CH_3OH afforded the cationic imido chloride **3**, which could be converted into the nitrido chloride **4** with sodium bis(trimethylsilyl)amide. From **3** and **4** the hydrido complexes of the type $Mo(H)(L)(depe)_2$ [L = N (**7**), $NBEt_3$ (**8**)] were obtained by the reaction with the hydride reagents $LiBH_4$ and $NaHBEt_3$. The hydridic character of the L_nM–H bond of **8** was determined by DQCC measurements (bond ionicity i = 81 %). Hydride reactivity studies were carried out on **7** and **8**; however, only **8** underwent hydride transfer reactions. **8** reacted with 4,4′-dichlorobenzophenone and acetophenone to afford the corresponding alkoxide complexes $Mo(NBEt_3)(OCHRR')(depe)_2$ [R, R′ = C_6H_4Cl (**10**); R = Me, R′ = Ph (**11**)]. The high propensity of **8** to undergo carbonyl insertion was documented further by reactions with CO_2 and carbonylmetal compounds. Conversion with CO_2 led to formation of the formato complex $Mo(NBEt_3)(OCHO)(depe)_2$ (**9**) and reactions with $Fe(CO)_5$ and $Re_2(CO)_{10}$ resulted in the formation of $Mo[(\mu\text{-}OCH)Fe(CO)_4](NBEt_3)(depe)_2$ (**12**) and $Mo[(\mu\text{-}OCH)Re_2(CO)_9](NBEt_3)(depe)_2$ (**13**). X-ray diffraction studies were carried out on **1**–**4**, **6**, **8**–**10** and **12**–**14**.

Introduction

For various homogeneous catalyses the activation of L_nM–H bonds[1–13] (M = transition metal) plays a decisive role. Insertion reactions of these bonds with unsaturated molecules are strongly dependent on the ancillary ligand sphere.[14] An increasing number of strongly σ-donating *cis*-phosphane substituents are expected to enhance the electron density on the metal center and on the hydrido ligand.[15] The ligand *trans* to the hydrido ligand is attributed a crucial *trans* influence. In a DFT study[16] the three complexes $LW(H)(dmpe)_2$ with L = NO, CH and N were compared and analyzed according to their various *trans* influences. The L_nM–H bond strength was found to decrease in the order NO > CH > N suggesting in this order increasing hydride transfer activity.

The nitrido ligand (N^{3-})[21–23] is regarded as a strong *trans*-influence ligand and a very strong π-donor; similar in this property may only be the isoelectronic oxo ligand. A combined experimental and theoretical study[24] has compared the Cr–L bonds with L = O_{oxo}, $N_{nitrido}$ and $C_{carbyne}$. From a natural bond orbital analysis, bond lengths and topological analyses of the total electron density, the bond order and the total binding interaction of this multiple bond is in the order Cr–N > Cr–O > Cr–C. The nitrido moiety is therefore expected to display an additional nucleophilic behaviour for early and middle transition metal complexes in high oxidation states.[25] The reactivity patterns of related hydrido complexes with *trans* ligands L = NO and CMes were reported earlier so that it remains to study the influence of the nitrido ligand.[14,17–20]

We describe here the synthesis of molecules based on nitrido ligands such as $Mo(H)(L)(depe)_2$ (L = N and $NBEt_3$) and we present also reactivity studies carried out with the $Mo(H)(NBEt_3)(depe)_2$ complex.

Results and Discussion

Hydrido Nitrido Complexes

A common route to access nitrido complexes consists of the decomposition of (azido)metal complexes. The synthetic route described in this paper was thus largely inspired by the initial work of Chatt and Dilworth[26] with some modifications developed in the group of Pickett.[27] For the synthesis of $Mo(N_2)_2(depe)_2$ (**1**) we applied the procedure described by George and Noble[28] which utilizes the reduction of $MoCl_5$ with sodium amalgam followed by the addition of the phosphane ligand under dinitrogen. The bis(dinitrogen) species **1** was obtained in 69% yield and characterized by an X-ray diffraction study (crystallographic data for **1** in the Supporting Information). The de-

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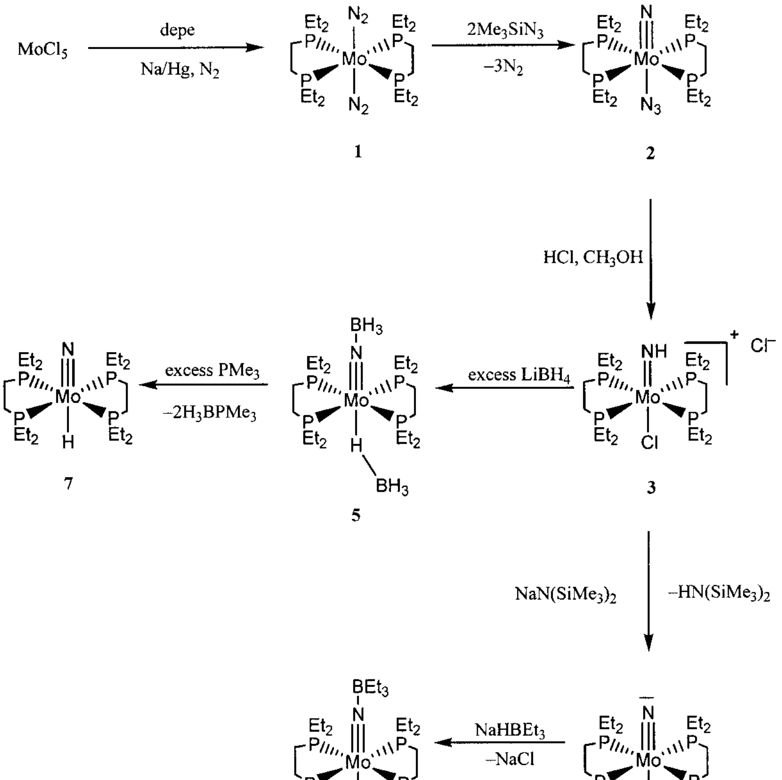
sired nitrido function was formed by treatment of **1** with trimethylsilyl azide[29,30] to yield the known compound $Mo(N)(N_3)(depe)_2$ (**2**). The imido derivative $[Mo(Cl)(NH)(depe)_2][Cl]$ (**3**) was then produced by protonation of **2**, dissolved in methanol, with a small amount of aqueous concentrated hydrochloric acid in CH_3OH.

Suitable crystals of **2** and **3** for X-ray diffraction studies were grown from a saturated THF solution at –30 °C (crystallographic data for both complexes are available in the Supporting Information).

According to literature[26,31,32] the imido group can be deprotonated by a suitable base. In this study sodium bis(trimethylsilyl)amide in toluene was used, which prevents side reactions and leads to higher yields[32] of the nitrido species $Mo(Cl)(N)(depe)_2$ (**4**) (Scheme 1).

The structure of **4** was additionally confirmed by an X-ray diffraction analysis (Figure 1) using a single crystal obtained by cooling of a saturated toluene solution to –30 °C. Three independent molecules were found in the asymmetric unit. For all of which a pseudooctahedral geometry was observed with the two depe ligands in equatorial and the chloride ion and nitrido group in *trans* positions. The average of the Mo–N bonds of 1.699(5) Å is slightly shorter than those observed in similar $(R_2P–CH_2–CH_2–PR_2)_2(X)$-$Mo{\equiv}N$ complexes [1.79(2) Å for R = Ph, X = $N–N{\equiv}N$,[33] 1.704(6) Å for R = Ph, X = $N{\equiv}C–C(CN)=C(O)(CH_3)$[34] and 1.704(3) Å for R = Ph, X = $N{\equiv}C–C(H)=C(O)(Ph)$[35]] which confirms the triple bond character of this unit. The *trans* influence of the nitride group is demonstrated by a long Mo–Cl distance [average value 2.772(2) Å], which is by more than 0.3 Å longer in comparison with the unweighted mean value of 2.410 Å reported in the literature.[36]

The preparation of two types of hydrido nitrido complexes was achieved. Starting from **3**, the borohydride $Mo(\eta^1\text{-}HBH_3)(NBH_3)(depe)_2$ (**5**) was obtained when an excess of $LiBH_4$ in THF was applied. The ^1H NMR spectrum of **5** in $[D_8]THF$ revealed a broad quadruplet at δ = –2.90 ppm with a characteristic ^{11}B coupling ($^1J_{HB}$ = 88 Hz), which was assigned to the protons of the tetrahydroborate moiety. The ^{11}B NMR spectrum furthermore showed a quadruplet at δ = –15.9 ppm ($^1J_{HB}$ = 82 Hz) for the BH_3 unit on the nitrido group, and a quintuplet at δ = –44.6 ppm ($^1J_{HB}$ = 82 Hz) for the BH_4 unit. Presumably, the reaction to **5** proceeded via the intermediate $Mo(Cl)(NBH_3)(depe)_2$ (**6**), since the reaction of **3** with just 1 equiv. of $LiBH_4$ indeed yields **6**. In the ^1H NMR spectrum a broad signal appeared at δ = 2.4 ppm, which was attributed to the NBH_3 moiety. The ^{11}B NMR spectrum of **6** revealed one quadruplet at δ = –13.5 ppm for the NBH_3 unit and its $^{31}P\{^1H\}$ NMR spectrum displayed a singlet at δ = 49.0 ppm indicating the presence of the four chemically equivalent phosphorus nuclei. A unique crystal of **6** suitable for an X-ray diffraction analysis was obtained from a saturated THF solution at –30 °C. Figure 2 shows the molecular



Scheme 1.

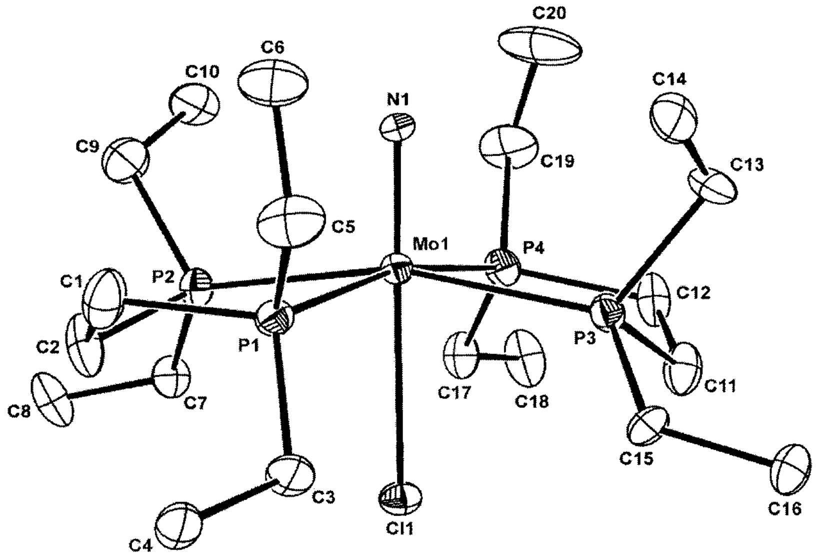


Figure 1. Molecular structure of **4**; only one of the three independent molecules is shown. Selected bond lengths [Å] and angles [°]: Mo1–N1 1.690(5), Mo1–Cl1 2.7901(19), N1–Mo1–Cl1 177.6(2) (molecule 1), Mo2–N2 1.684(5), Mo2–Cl2 2.7406(17), N2–Mo2–Cl2 175.06(18) (molecule 2) and Mo3–N3 1.722(5), Mo3–Cl3 2.7859(19), N3–Mo3–Cl3 174.23(19) (molecule 3). The displacement ellipsoids are of 20% probability and all hydrogen atoms have been omitted for clarity.

structure of **6**. Disorder was recognized between the NBH_3 and Cl groups, which prevented an accurate comparison of the bond parameters of **4** and **6**. On a rough scale, however, a significantly shorter Mo–Cl bond of 2.621(2) Å seems to be present in **6**, which speaks for a weaker *trans* influence of the NBH_3 unit in **6** with respect to that of the nitrido group in **4**.

Treatment of the borohydride species **5** with an excess of PMe_3 in toluene at 120 °C for 11 d resulted in the formation of the desired hydride $Mo(H)(N)(depe)_2$ (**7**). The ^1H NMR spectrum of **7** in C_6D_6 displayed at room temperature, among other resonances, that of the hydrido ligand as a quintuplet at δ = –5.99 ppm ($^2J_{HP}$ = 30 Hz). The $^{31}P\{^1H\}$ NMR spectrum reveals a singlet at δ = 80.6 ppm.

The $NBEt_3$-substituted hydrido complex **8** was obtained from the nitrido chloride **4** by treatment with a slight excess of the hydride reagent $NaHBEt_3$ in THF at room temperature for 15 h. Due to the considerable basicity of the ter-

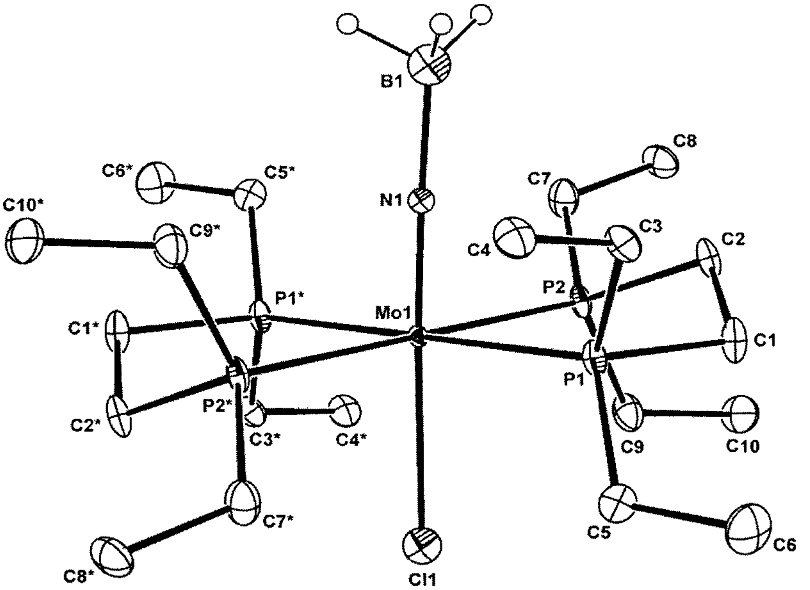


Figure 2. Molecular structure of **6** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N1 1.656(4), Mo1–Cl1 2.621(2), N1–B1 1.62(1); N1–Mo1–Cl1 177.49(13), B1–N1–Mo1 177.9(4). The molybdenum center lies on a special position (inversion center) and half of the molecule is reproduced by the symmetry operation 1 – *x*, 1 – *y*, 1 – *z* (the symmetry-related atoms are labeled with an asterisk). The hydrogen atoms of the BH_3 group have been refined with soft B–H distance restraints. The NBH_3/Cl disorder and selected hydrogen atoms have been omitted for clarity.

minal nitrido group the "leftover" BEt_3 moiety is scavenged after H^- transfer to the Mo center. The ^1H NMR spectrum of **8** shows a characteristic resonance for the hydrido ligand as a quintuplet at $\delta = -6.23$ ppm ($^2J_{HP} = 36$ Hz). The presence of the *N*-bound BEt_3 group was confirmed by a CH_2 resonance in the ^1H NMR spectrum appearing as a 1:3:3:1 quadruplet at $\delta = 0.86$ ppm ($^3J_{HH} = 8$ Hz) and a triplet for the Me groups at $\delta = 1.36$ ppm ($^3J_{HH} = 8$ Hz). In the ^{13}C NMR spectrum the signal of the CH_2 groups of the BEt_3 moiety could not be detected. Their chemical shift at $\delta = 18.9$ ppm could only be extracted from a C–H correlation spectrum of **8**.

The molecular structure of **8** was confirmed by an X-ray diffraction analysis. It exhibits pseudooctahedral coordination of the Mo center with the two depe ligands in equatorial positions and the hydrido ligand and the NBH_3 group *trans* to each other (Figure 3). The hydride atom was found in the difference electron density map. It could be refined isotropically (0.022 Å^2). The Mo–H bond length of 1.85(2) Å compares well with that observed for the $Mo(H)(CO)(NO)(PMe_3)_3$ complex [1.84(3) Å].[19] The Mo–N bond of 1.7571(14) is longer than in **4** [1.698(5) Å], presumably due to the attached BEt_3 group which apparently reduces the strength of the metal–nitrogen triple bond.

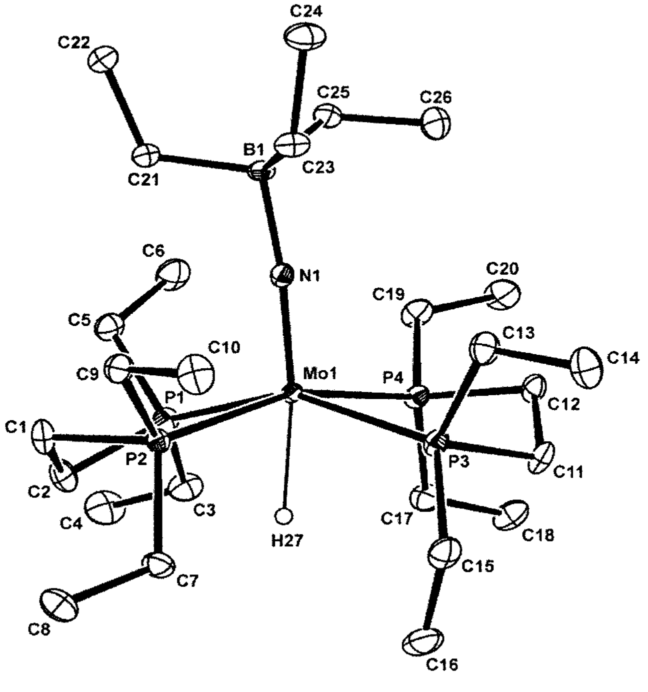


Figure 3. Molecular structure of **8** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N1 1.7571(14), Mo1–H27 1.85(2), N1–B1 1.568(2), N1–Mo1–H27 171.2(7), B1–N1–Mo1 173.69(14). All hydrogen atoms have been omitted for clarity, except the hydrido atom H27 for which the positional parameters were freely refined.

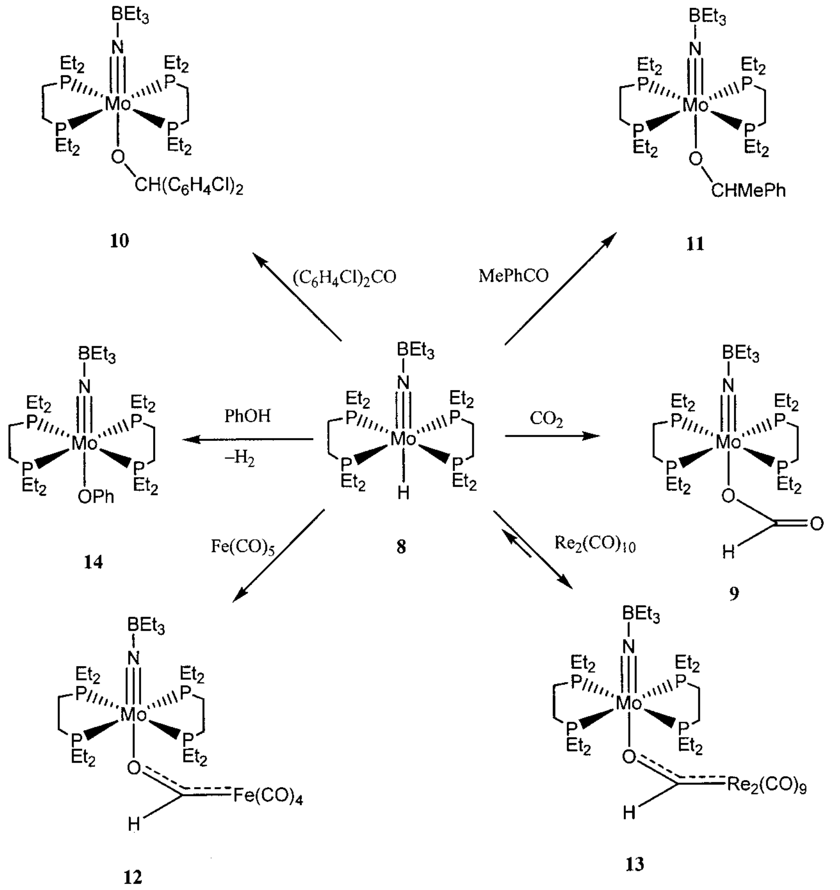
Hydridic Character of the *trans*-$Mo(H)(NBEt_3)(depe)_2$ Complex 8

Different approaches to classify the L_nM–H bond in terms of its hydridic character are based either on kinetic or thermodynamic studies of hydride transfer reactions. Cheng and Bullock[37] determined kinetic hydridicities by the reaction of L_nM–H bonds (M = transition metal) with the trityl cation. The work of Sarker and Bruno[38] rely on the equilibration of both types of species to establish a thermodynamic scale of hydridicities. Bond ionicities may also be taken as an indicator for the hydridic character of the L_nM–H bond. We used ^2H NMR spectroscopy to determine the deuterium quadrupole coupling constant (DQCC) of the D nucleus by measuring the temperature-dependent T_{1min} relaxation time in [H_8]toluene[39,40] and also by calculation of the DQCC from the "Pake doublet" appearing in the static solid-state NMR spectrum, preferably at low temperatures. For these experiments the deuterium derivative $Mo(D)(NBEt_3)(depe)_2$ (**8a**) had to be prepared using LiDBEt$_3$ instead of $NaHBEt_3$. According to the T_{1min} method, the DQCC of the deuteride **8a** was calculated to be 43 ± 1 kHz. The ionicity of the Mo–D(H) is thus 81.0 ± 0.4% and stresses the strong polarity of the Mo–D bond in **8a**. This bond ionicity belongs to the largest ionicities reported for transition metal hydrides.[41] From the solid-state ^2H NMR spectra a Δ value of the "Pake doublet" of 31.1 kHz is obtained, from which the DQCC was calculated to be 42 ± 1 kHz corresponding to a bond ionicity of 81.7 ± 0.5% very close to the value obtained by the T_{1min} method.

Hydride Transfer Reactions of $Mo(H)(N)(depe)_2$ (7) and *trans*-$Mo(H)(NBEt_3)(depe)_2$ (8)

Very much to our surprise, the hydride **7** turned out to be very unreactive. It did not react with ketones or carbonylmetal compounds and produced a mixture of unidentified products in the presence of CO_2. The reason for this is yet unclear, especially in view of the fact that the very related derivative **8**, distinguished from **7** by an additional Lewis acid bound to the nitrido ligand, showed various hydride transfer reactions.

The Mo–H bond of **8** was shown to be highly polarized and at least in a kinetic sense this complex seemed to be prone to undergo hydride transfer reactions, i.e. insertions with a wide variety of unsaturated compounds such as CO_2,[42–48] ketones and carbonylmetal compounds (Scheme 2). Reaction of **8** with an excess of CO_2 (450 mbar at –196 °C) in [D_8]toluene indeed proceeded smoothly at room temeperature. The reaction was complete after a few minutes and the *O*-formate product $Mo(OCHO)(NBEt_3)(depe)_2$ (**9**) was isolated in 70% yield as analytically pure yellow crystals after recrystallisation from diethyl ether solution. The formate group of **9** displayed a singlet resonance at $\delta = 8.04$ ppm in the ^1H NMR spectrum and a singlet resonance at $\delta = 166.0$ ppm in the ^{13}C NMR spectrum. The IR spectrum of **9** revealed two intense bands at 1611 and 1320 cm^{-1} for the formate ligand, in accordance with other η^1-formate complexes reported in the literature.[49,50] The structure of **9** was finally confirmed by an X-ray diffraction analysis (Figure 4).



Scheme 2.

The molybdenum centre adopts a pseudooctahedral geometry, with the $NBEt_3$ moiety and the η^1-formato ligand *trans* to each other. The structure revealed an Mo–O bond length of 2.214(2) Å.[18,50,51] The Mo–N and N–B bond lengths of 1.713(3) Å and 1.609(5) Å, respectively, are similar to those of **10** and **14**.

Reactions of **8** with 4,4′-dichlorobenzophenone and acetophenone were completed at 60 °C in 1 d and at room temperature in 3 d, respectively, to afford the corresponding alkoxide complexes *trans*-$Mo(OCHRR')(NBEt_3)(depe)_2$ [R = R′ = *p*-C_6H_4Cl (**10**); R = Ph, R′ = Me (**11**)]. 4,4′-Dichlorobenzophenone was chosen as a model reagent for disubstituted aromatic ketones, because of difficulties faced in the reaction of **8** with the parent benzophenone where two products were obtained, which could not be separated. In the ^1H NMR spectrum compound **10** shows a singlet at δ = 4.68 ppm and a characteristic signal at δ = 83.1 ppm in the ^{13}C NMR spectrum, both being attributed to the Mo–OCH moiety. In a similar manner, the OCH moiety of complex **11** was identified by a quadruplet at δ = 4.11 ppm ($^3J_{HH}$ = 6.3 Hz) in the ^1H NMR spectrum and by a singlet at δ = 75.1 ppm in the ^{13}C NMR spectrum. Single crystals of **10** suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of **10** in diethyl ether to –30 °C.

As shown in Figure 5, the molybdenum center of **10** exhibits a pseudooctahedral coordination environment similar to that of the complexes mentioned before. This structure shows an Mo–O bond length of 2.1781(16) Å, in the range of those reported in related structures.[19,52] The Mo1–N1 bond length of 1.733(2) Å falls into the range of those observed for **8** and **9**, while the N1–B1 bond length of 1.612(4) is similar to that in **9**.

The insertion of CO into an activated L_nM–H bond could result in the formation of a formyl species. This reaction has been proposed to be a key step in the homogeneous hydrogenation of CO. However, the direct product of CO insertion into an L_nM–H bond to give a metal-bound formyl group has only rarely been observed,[53–57] because in most cases this step is thermodynamically not favourable. Despite this, metal-bound CO was found to insert into strongly polar L_nM–H bonds. Insertion of **8** with $Fe(CO)_5$ and $Re_2(CO)_{10}$ was thus attempted affording the μ-formyl complexes *trans*-$Mo[(\mu\text{-}OCH)Fe(CO)_4](NBEt_3)(depe)_2$ (**12**) and *trans*-$Mo[(\mu\text{-}OCH)Re_2(CO)_9](NBEt_3)(depe)_2$ (**13**). Compound **12** was isolated as yellow crystals after recrystallisation from a saturated toluene solution. In contrast to the reaction with $Fe(CO)_5$, the reaction with $Re_2(CO)_{10}$ in toluene reaches an equilibrium after 2 d which is strongly shifted to the formyl side. Analytically pure

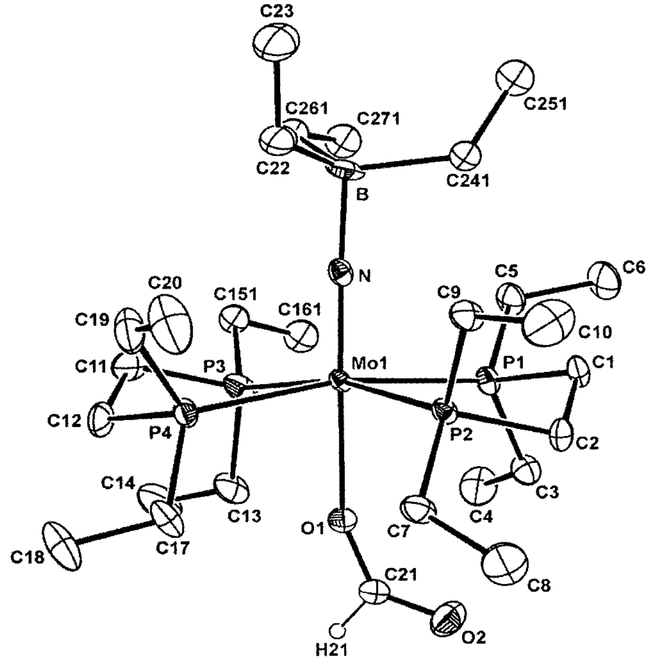


Figure 4. Molecular structure of **9** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N 1.713(3), Mo1–O1 2.214(2), N–B 1.609(5), O1–C21 1.234(4), Mo1–*N*–B 177.5(3), N–Mo1–O1 179.07(13), Mo1–O1–C21 157.6(3). Selected hydrogen atoms and the disordered ethyl groups on the phosphorus atom P3 and on the boron atom have been omitted for clarity.

orange crystals of **13** were obtained by crystallization from toluene. Among other resonances, the ^1H NMR spectra of **12** and **13** show characteristic H_{formyl} signals at δ = 13.78 ppm and at δ = 14.91 ppm in a typical chemical shift region reported for similar complexes.[14,17,19,52] The ^{31}P NMR spectrum displays a singlet for the four equivalent phosphorus nuclei at δ = 52.2 ppm and at δ = 54.4 ppm for **12** and **13**, respectively. In the low-field region the ^{13}C NMR spectra consist of a broad signal for the C_{formyl} atom at δ = 293.2 ppm and δ = 289.5 ppm for **12** and **13**, respectively. In the IR spectrum of **12** the ν(CO) bands of the $Fe(CO)_4$ moiety appear at 2020, 1966 and 1870 cm^{-1} and in the IR spectrum of **13** seven bands at 2094, 2070, 2025, 2007, 1969, 1935 and 1902 cm^{-1} are found, which were assigned to the ν(CO) vibrations of the $Re_2(CO)_9$ unit.

The X-ray structures of **12** and **13** are presented in Figures 6 and 7. Both coordination geometries around the Mo centers possess a distorted octahedral arrangement. The μ-formyl bond lengths in **12** [1.219(3) Å] and **13** [1.250(4) Å] are noticeably different, with a longer separation in the rhenium complex **13** indicating a stronger π-donation of the $Re_2(CO)_9$ fragment.

The potential for hydrogenations using **8** was tested by the reaction of the hydride with acetone in the presence of a proton donor (PhOH) simulating a stoichiometric "ionic hydrogenation". The reaction of **8** with the phenol alone was so fast that instantaneous formation of H_2 and the phenoxy complex **14** was observed (signal at δ = 4.45 ppm in the ^1H NMR spectrum). A crystal of **14** suitable for an X-ray analysis was obtained from a saturated diethyl ether solution at –30 °C. The molecular structure of **14** shows the molybdenum atom in pseudo-octahedral environment with the phenoxy[58] group and the Et_3BN ligand *trans*-disposed to each other (Figure 8).

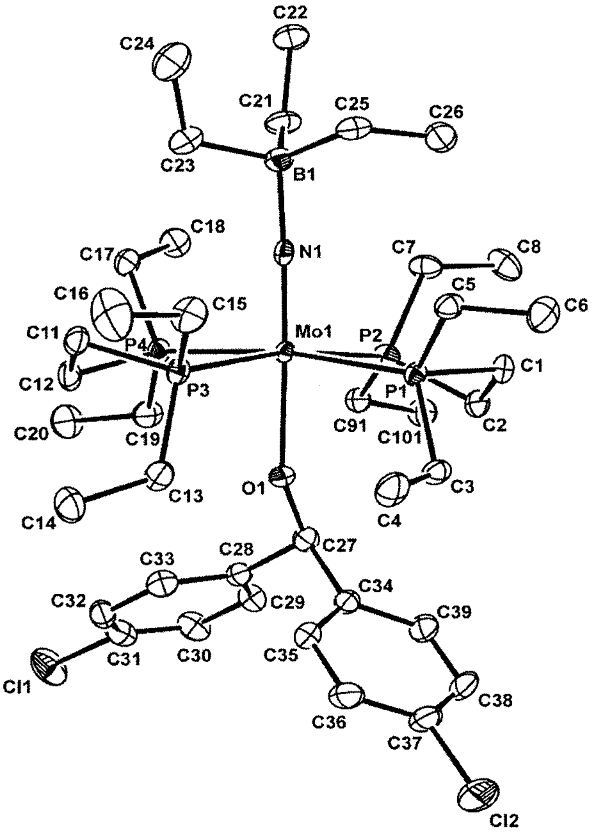


Figure 5. Molecular structure of **10** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N1 1.732(2), N1–B1 1.612(4), Mo1–O1 2.1781(16), Mo1–N1–B1 177.1(2), N1–Mo1–O1 177.39(8), Mo1–O1–C27 147.98(16). All hydrogen atoms and the disordered ethyl group of the phosphorus atom P2 have been omitted for clarity.

The hydrogenation of cyclohexene was also attempted using **8** without the presence of an acidic substrate. A Young NMR tube was pressurized with 1700 mbar H_2 in the presence of complex **8** (1%). After 12 d at 110 °C, 94% of the cyclohexene was found to be hydrogenated to cyclohexane. The ^1H NMR spectrum of the reaction mixture showed that the typical signals of the cyclohexene starting material (δ = 5.59, 1.85, 1.46 ppm) decreased, while the characteristic resonance for cyclohexane (δ = 1.34 ppm) appeared. The presence of the cyclohexane was further confirmed by GC-MS. However, **8** could not be recovered. The ^{31}P NMR showed the presence of the free depe phosphane (δ = –17.9 ppm) among several unidentified signals indicating that **8** is a precursor to the irreversibly formed catalytically active species, which presumably coordinates only one depe ligand.

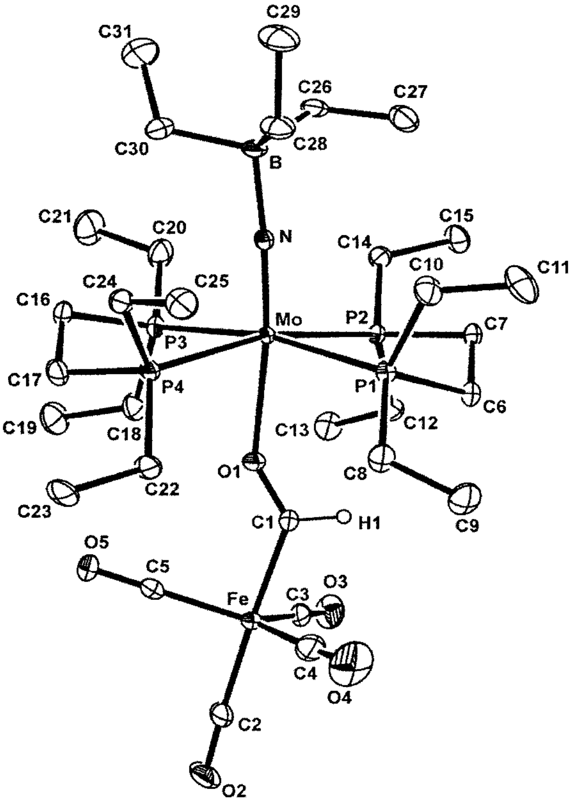


Figure 6. Molecular structure of **12** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo–N 1.717(2), Mo–O1 2.3044(17), N–B 1.615(4), C–O 1.219(3), Fe–C 1.933(3), Mo–O1–C1 145.10(18), Fe–C1–O1 132.0(2), N–Mo–O1 173.27(9), Mo–N–B 175.7(2). All hydrogen atoms, except H1, and the co-crystallized solvent molecule of toluene have been omitted for clarity.

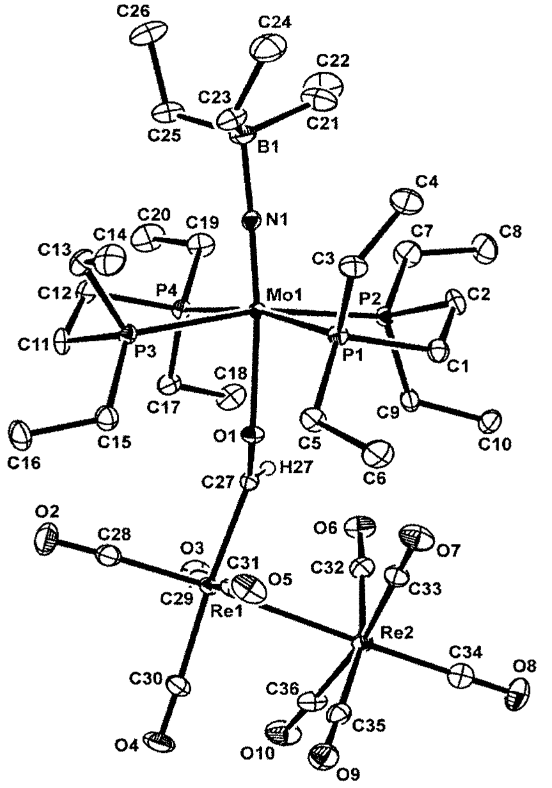


Figure 7. Molecular structure of **13** (ellipsoids are drawn at the 40% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N1 1.712(3), Mo1–O1 2.350(2), N1–B1 1.625(5), C27–O1 1.250(4), Re1–C27 2.137(4), Re1–Re2 3.0511(3), Mo1–O1–C27 139.4(2), Re1–C27–O1 130.6(3), C27–Re1–Re2 91.26(10), N1–Mo1–O1 173.63(12), Mo1–N1–B1 176.0(3). All hydrogen atoms, except H27, have been omitted for clarity.

Conclusion

Two transition metal hydride complexes of the type Mo(H)(L)(depe)$_2$ [L = N (**7**), NBEt$_3$ (**8**)] were prepared. Since a high propensity for insertion reactions was found for **8**, but not for **7**, hydridicity and reactivity of **8** were investigated in detail. Even though this difference in chemical behaviour is yet unexplained, it indicates that slight alterations in the coordination sphere may cause rather pronounced reactivity changes of the L$_n$M–H bond; an important circumstance for any hydride tuning efforts.

Experimental Section

General: Reagent grade benzene, toluene, pentane, diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl prior to use. MeOH was dried and distilled from Mg. Literature procedures were used to prepare the following compounds: 1,2-bis(diethylphosphanyl)ethane (depe)[59] and PMe$_3$.[60] Other reagents were purchased and used without further purification. All the manipulations were carried out under nitrogen using Schlenk techniques or a dry glovebox. IR spectra were obtained with a Bio-Rad FTS-45 instrument and Raman spectra were obtained with a Renishaw Labram Raman spectrometer. Mass spectra were obtained with a Finnigan-MAT-8400 spectrometer. Gas chromatography-mass spectra (GC-MS) were recorded with a Varian-Chrompack CP-3800 gas chromatograph equipped with a Saturn 2000 electron impact mass spectrometer (EI-MS). The samples were carried by an He flow through a CP-SIL 8 CB-MS FS 30 × 25 (.25) column; flow: 1 mL/ min, split: 100:1, EI: 70 eV, isothermal method at 30 °C. NMR spectra were measured with a Varian Mercury 200 spectrometer at 81.0 MHz for $^{31}P\{^1H\}$, with a Varian Gemini 300 spectrometer at 300.1 MHz for ^1H, 121.5 MHz for $^{31}P\{^1H\}$, 75.4 MHz for $^{13}C\{^1H\}$ and 96.2 MHz for $^{11}B\{^1H\}$ and with a Bruker-DRX-500 spectrometer at 500.2 MHz for ^1H, 202.5 MHz for $^{31}P\{^1H\}$, 125.8 MHz for $^{13}C\{^1H\}$, 36.2 MHz for ^{14}N and 32.5 MHz for ^{95}Mo. Chemical shifts for ^1H and ^{13}C are given in ppm relatively to TMS (SiMe$_4$), the $^{31}P\{^1H\}$ NMR spectra were referenced to 98% external H$_3$PO$_4$, ^{11}B relative to Et$_2$O·BF$_3$, ^{14}N relative to CH$_3$NO$_2$ and ^{95}Mo relative to MoO$_4^{2-}$. Elemental analyses: Leco CHN(S)-932 instrument.

Preparation of *trans*-Mo(N$_2$)$_2$(depe)$_2$ (1): Ligand depe (0.744 g, 3.61 mmol) was added dropwise to 20 mL of a THF suspension of 1% Na amalgam under nitrogen. Then sublimed MoCl$_5$ (0.410 g, 1.5 mmol) was added and the brown solution was stirred for 18 h. The solution was filtered twice through Celite which was then rinsed with toluene. The solvent was removed under vacuum and the resulting precipitate dissolved in 30 mL of toluene. The solution was filtered further twice through Celite, and brought to a volume of 12 mL under vacuum; 24 mL of MeOH was added to precipitate the product at –30 °C within 15 h. The orange needles were filtered off, washed with MeOH and then dried under vacuum. Yield of **1**:

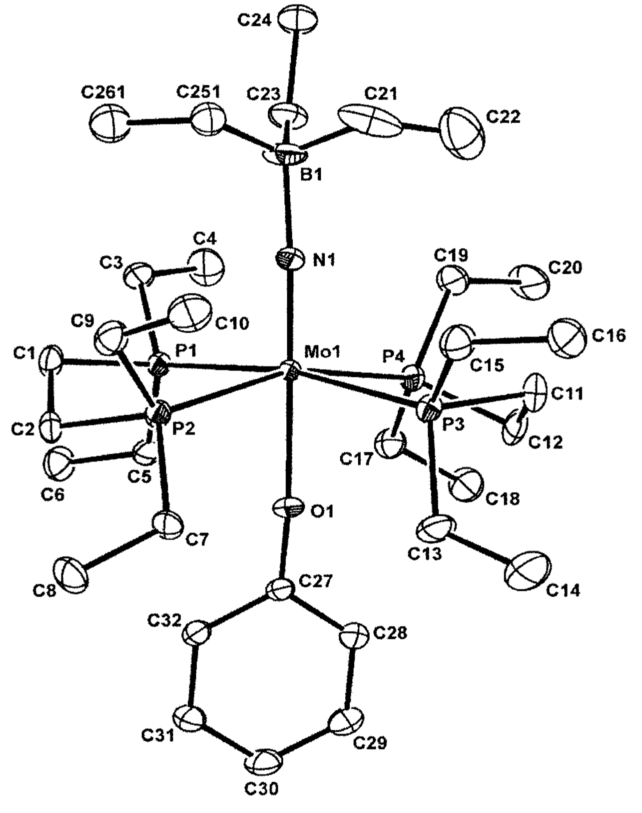


Figure 8. Molecular structure of **14** (ellipsoids are drawn at the 30% probability level). Selected bond lengths [Å] and angles [°]: Mo1–N1 1.719(2), Mo1–O1 2.1656(18), N1–B1 1.603(4), Mo1–O1–C27 175.43(19), N1–Mo1–O1 178.05(10), Mo1–N1–B1 176.8(2). All hydrogen atoms and the disordered ethyl group on the boron atom have been omitted for clarity.

0.592 mg, 1.04 mmol, 69%. ^{1}H NMR (C$_6$D$_6$, 298 K, 300.1 MHz): δ = 1.83 (m, 16 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.35 [m, 8 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.09 (m, 24 H, $\mathrm{PCH_2C}H_3$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 298 K, 121.5 MHz): δ = 56.7 (s) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K, 75.4 MHz): δ = 23.7 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 21.4 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 8.7 (m, $\mathrm{PCH_2}C\mathrm{H_3}$) ppm. IR (KBr): ṽ = 1921 [ν$_{\mathrm{asym}}$(N$_2$)] cm^{-1}. Raman: ṽ = 1997 [ν$_{\mathrm{sym}}$(N$_2$)] cm^{-1}. C$_{20}$H$_{48}$MoN$_4$P$_4$ (564.45): calcd. C 42.56, H 8.57, N 9.93; found C 42.86, H 8.44, N 9.88.

Preparation of *trans*-Mo(N)(N$_3$)(depe)$_2$ (2): Complex **1** (0.507 mg, 0.90 mmol) was dissolved in 30 mL of THF in a round-bottomed flask and trimethylsilyl azide (0.32 mL, 2.43 mmol) was added. The mixture was refluxed for at least 1 h. The reddish solution was filtered through Celite and concentrated under vacuum. The solid was rinsed with pentane and dried under vacuum to afford a brown solid. Yield of **2**: 0.449 mg, 0.79 mmol, 88%. ^{1}H NMR (C$_6$D$_6$, 293 K, 300.1 MHz): δ = 2.11–1.73 (m, 16 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.52 [br. m, 4 H, P(CH$_2$)$_2$P], 1.36 [br. m, 4 H, P(CH$_2$)$_2$P], 1.20 (m, 12 H, $\mathrm{PCH_2C}H_3$), 1.02 (m, 12 H, $\mathrm{PCH_2C}H_3$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K, 121.5 MHz): δ = 59.2 (br. s) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K, 75.4 MHz): δ = 22.2 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 21.8 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 19.0 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 8.5 (s, $\mathrm{PCH_2}C\mathrm{H_3}$), 7.5 (s, $\mathrm{PCH_2}C\mathrm{H_3}$) ppm. IR (ATR): ṽ = 2022 [ν$_{\mathrm{asym}}$(N$_3$)], 977 [ν(Mo≡N)] cm^{-1}. Raman: ṽ = 1342 [ν$_{\mathrm{sym}}$(N$_3$)] cm^{-1}. C$_{20}$H$_{48}$MoN$_4$P$_4$ (564.45): calcd. C 42.56, H 8.57, N 9.93; found C 42.92, H 8.45, N 9.56.

Preparation of *trans*-[Mo(Cl)(NH)(depe)$_2$][Cl] (3): Compound **2** (0.412 g, 0.73 mmol) was dissolved in 15 mL of MeOH and a few drops of 32% aqueous HCl were added. A darkening of the red solution was observed. The solution was stirred for 15 min and then the solvent was removed under vacuum. The precipitate was dissolved in THF, the solution filtered through Celite, concentrated under vacuum, and the residue washed three times with pentane and dried under vacuum to yield a red powder. Yield of **3**: 349 mg, 0.59 mmol, 80%. ^{1}H NMR ([D$_8$]THF, 295 K, 500.2 MHz): δ = 2.07 (m, 16 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.92 [br. m, 8 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.21 (m, 24 H, $\mathrm{PCH_2C}H_3$) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF, 295 K, 202.5 MHz): δ = 47.5 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF, 295 K, 125.8 MHz): δ = 23.2 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 19.0 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 8.3 (s, $\mathrm{PCH_2}C\mathrm{H_3}$) ppm. C$_{20}H_{49}Cl_2$MoNP$_4$ (594.35): calcd. C 40.42, H 8.31, N 2.36; found C 40.03, H 7.97, N 2.07.

Preparation of *trans*-Mo(Cl)(N)(depe)$_2$ (4): Compound **3** (203.6 mg, 0.34 mmol) was suspended in 15 mL of toluene and a 0.6 M solution of NaN(SiMe$_3$)$_2$ in toluene (1.14 mL, 0.68 mmol) was added. The precipitate was dissolved and the solution stirred overnight. The brown solution was filtered through Celite and concentrated under vacuum. Then **4** was extracted with pentane and the solution concentrated under vacuum to yield a brown powder. Yield of **4**: 123.5 mg, 0.22 mmol, 64%. ^{1}H NMR (C$_6$D$_6$, 293 K, 500.2 MHz): δ = 2.38 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.88 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.80 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.75 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.64 [br. m, 4 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.41 [br. m, 4 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.27 (m, 12 H, $\mathrm{PCH_2C}H_3$), 1.04 (m, 12 H, $\mathrm{PCH_2C}H_3$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K, 121.5 MHz): δ = 56.0 (s) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K, 125.8 MHz): δ = 22.4 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 21.7 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 19.4 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 9.0 (s, $\mathrm{PCH_2}C\mathrm{H_3}$), 7.8 (s, $\mathrm{PCH_2}C\mathrm{H_3}$) ppm. IR (KBr): ṽ = 984 [ν(Mo≡N)] cm^{-1}. Raman: ṽ = 915 [ν(Mo≡N)] cm^{-1}. MS (EI): *m*/*z* = 560 [M$^+$], 353 [M$^+$ – 1 depe]. C$_{20}$H$_{48}$ClMoNP$_4$ (557.88): calcd. C 43.06, H 8.67, N 2.51; found C 43.35, H 8.53, N 2.63.

Preparation of *trans*-Mo(η^1-HBH$_3$)(NBH$_3$)(depe)$_2$ (5): Complex **3** (1.0192 g, 1.71 mmol) was mixed with LiBH$_4$ (28.8 mg, 8.59 mmol), dissolved in 50 mL of THF. Evolution of gas, assumed to be H$_2$, was observed and the mixture was stirred overnight. The solution was filtered through Celite and concentrated under vacuum. The precipitate was dissolved in toluene, the solution filtered through Celite twice and concentrated under vacuum to afford a brown powder. Yield of **5**: 502 mg, 0.91 mmol, 53%. ^{1}H NMR ([D$_8$]THF, 293 K, 500.2 MHz): δ = 2.17–1.93 (m, 16 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.83 [br. m, 8 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.44 (br., 3 H, $\mathrm{B}H_3$), 1.25 (m, 12 H, $\mathrm{PCH_2C}H_3$), 1.18 (m, 12 H, $\mathrm{PCH_2C}H_3$), –2.9 (q, 4 H, $H\mathrm{B}H_3$, $^1J_{\mathrm{HB}}$ = 82 Hz) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF, 293 K, 202.5 MHz): δ = 47.0 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF, 293 K, 125.8 MHz): δ = 22.5 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 19.8 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 19.4 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 9.1 (s, $\mathrm{PCH_2}C\mathrm{H_3}$), 8.6 (s, $\mathrm{PCH_2}C\mathrm{H_3}$) ppm. ^{11}B NMR ([D$_8$]THF, 293 K, 160.5 MHz): δ = –15.9 (q, 1 B, $\mathrm{N}B\mathrm{H_3}$, $^1J_{\mathrm{HB}}$ = 88 Hz), –44.62 (quint, 1 B, $\mathrm{H}B\mathrm{H_3}$, $^1J_{\mathrm{HB}}$ = 82 Hz) ppm. IR (ATR): ṽ = 2290 [ν(B–H)] cm^{-1}. C$_{20}$H$_{55}$B$_2$MoNP$_4$ (551.11): calcd. C 43.59, H 10.06, N 2.54; found C 43.27, H 10.35, N 2.24.

Preparation of *trans*-Mo(Cl)(NBH$_3$)(depe)$_2$ (6): Compound **3** (50.7 mg, 0.085 mmol) was mixed with LiBH$_4$ (1.85 mg, 0.085 mmol), dissolved in 15 mL of THF. H$_2$ gas evolution was observed and the mixture was stirred overnight. The solution was filtered through Celite and concentrated under vacuum; the precipitate was dissolved in toluene, the solution filtered twice again through Celite and concentrated under vacuum to yield a yellow powder. Yield of **6**: 39.2 mg, 0.069 mmol, 80%. ^{1}H NMR (C$_6$D$_6$, 293 K, 300.1 MHz): δ = 2.4 (q, 3 H, $\mathrm{B}H_3$, $^1\mathrm{J}_{\mathrm{HB}}$ = 85 Hz), 2.17–1.93 (m, 16 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 1.83 [br. m, 8 H, $\mathrm{P(C}H_2)_2\mathrm{P}$], 1.18 (m, 12 H, $\mathrm{PCH_2C}H_3$), 0.95 (m, 12 H, $\mathrm{PCH_2C}H_3$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K, 121.5 MHz): δ = 49.0 (s) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K, 75.4 MHz): δ = 21.7 [m, $\mathrm{P(}C\mathrm{H_2)_2P}$], 19.3 (m, $\mathrm{P}C\mathrm{H_2CH_3}$), 18.1 (m, PCH_2CH_3), 9.1 (s, PCH_2CH_3), 8.2 (s, PCH_2CH_3) ppm. ^{11}B NMR ([H$_8$]THF, 293 K, 96.2 MHz): δ = –13.5 (q, 1 B, NBH_3, $^1J_{HB}$ = 95 Hz) ppm. IR (ATR): $\tilde{\nu}$ = 2287 [ν(B–H)] cm^{-1}. $C_{20}H_{51}BClMoNP_4$ (571.72): calcd. C 42.01, H 8.99, N 2.45; found C 41.88, H 8.95, N 2.23.

Preparation of *trans*-Mo(H)(N)(depe)$_2$ (7): A mixture of **5** (502 mg, 0.91 mmol) with an excess of PMe_3 (1.41 mL, 13.6 mmol) was dissolved in 40 mL of toluene in an autoclave. The autoclave was placed in an oil bath at 120 °C for 11 d. The solution was concentrated under vacuum; **7** was extracted into pentane, the solution filtered through Celite and concentrated under vacuum to yield a red oil. Yield of **7**: 347.5 mg, 0.66 mmol, 73%. ^{1}H NMR (C_6D_6, 293 K, 500.2 MHz): δ = 1.54 [br. m, 24 H, $P(CH_2)_2P$, PCH_2CH_3], 1.14 (br. m, 24 H, PCH_2CH_3), –5.99 (quint, 1 H, Mo–H, $^2J_{PH}$ = 30 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 202.5 MHz): δ = 80.6 (s, $^1J_{PMo}$ = 102 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.8 MHz): δ = 28.2 [br., PCH_2CH_3, $P(CH_2)_2P$], 9.3 (br., PCH_2CH_3) ppm. $^{14}N\{^1H\}$ NMR (C_6D_6, 293 K, 36.2 MHz): δ = –71.6 (s) ppm. ^{95}Mo NMR (C_6D_6, 293 K, 32.5 MHz): δ = –2062 (quint, $^1J_{PMo}$ = 102 Hz) ppm. MS (EI): *m*/*z* = 526 [M$^+$]. $C_{20}H_{49}MoNP_4$ (523.4): calcd. C 45.89, H 9.44, N 2.68; found C 45.66, H 9.62, N 2.71.

Preparation of *trans*-Mo(H)(NBEt$_3$)(depe)$_2$ (8): Complex **4** (291.8 mg, 0.52 mmol) was dissolved in THF (40 mL) and a 1 M solution of $NaHBEt_3$ in THF (0.54 mL, 0.54 mmol) was added. The reaction mixture was stirred at room temperature for 1 d. The solvent was removed under vacuum and the precipitate was extracted into pentane, the solution filtered through Celite and concentrated under vacuum. The crude product was recrystallised from a saturated diethyl ether solution by cooling to –30 °C to afford yellow-orange crystals. Yield of **8**: 385.5 mg, 0.48 mmol, 92%. ^{1}H NMR (C_6D_6, 293 K, 500.2 MHz): δ = 2.18 (br. m, 8 H, PCH_2CH_3), 1.65 (br. m, 4 H, PCH_2CH_3), 1.48 [br. m, 4 H, $P(CH_2)_2P$], 1.37 [br. m, 4 H, $P(CH_2)_2P$], 1.36 (t, 9 H, BCH_2CH_3, $^3J_{HH}$ = 7.5 Hz), 1.25 (br. m, 4 H, PCH_2CH_3), 1.17 (m, 12 H, PCH_2CH_3), 0.77 (m, 12 H, PCH_2CH_3), 0.68 (q, 6 H, BCH_2CH_3, $^3J_{HH}$ = 7.5 Hz), –6.23 (quint, 1 H, Mo–H, $^2J_{PH}$ = 36 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 202.5 MHz): δ = 65.5 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.8 MHz): δ = 24.8 (m, PCH_2CH_3), 23.6 [m, $P(CH_2)_2P$], 23.5 (m, PCH_2CH_3), 18.9 (br., BCH_2CH_3), 12.7 (s, BCH_2CH_3), 9.2 (s, PCH_2CH_3), 8.1 (s, PCH_2CH_3) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 293 K, 160.5 MHz): δ = –1.7 (s, 1 B, $NBEt_3$) ppm. IR (ATR): $\tilde{\nu}$ = 1417 [ν(Mo–H)] cm^{-1}. $C_{26}H_{64}BMoNP_4$ (621.43): calcd. C 50.25, H 10.38, N 2.25; found C 50.18, H 10.49, N 2.22.

Preparation of *trans*-Mo(D)(NBEt$_3$)(depe)$_2$ (8a): Complex **8a** was obtained by an analogous procedure as for **8**, using $LiDBEt_3$ instead of $NaHBEt_3$. ^{2}H NMR ([H$_8$]toluene, 293 K, 76.79 MHz): δ = –6.51 (br.) ppm. $^{31}P\{^1H\}$ NMR ([H$_8$]toluene, 293 K, 202.5 MHz): δ = 65.1 (t, $^2J_{PD}$ = 5.4 Hz) ppm.

Preparation of *trans*-Mo[$^1\eta$-OC(O)H](NBEt$_3$)(depe)$_2$ (9): The hydrido complex **8** (42.4 mg, 0.068 mmol) was dissolved in 0.5 mL of [D$_8$]toluene in a Young NMR tube, which was put under 450 mbar of CO_2 at 77 K. The reaction mixture was warmed to room temperature. The solution became light orange and after 30 min the solvent and the excess of CO_2 were removed under vacuum. The compound was extracted into Et_2O and the solution filtered through Celite. Recrystallisation from Et_2O at –30 °C afforded yellow crystals. Yield of **9**: 31.9 mg, 0.048 mmol, 70%. ^{1}H NMR (C_6D_6, 293 K, 300.1 MHz): δ = 8.04 (s, 1 H, $OCHO$), 2.2 [br. m, 4 H, $P(CH_2)_2P$], 2.10 (br. m, 8 H, PCH_2CH_3), 1.64 [br. m, 4 H, $P(CH_2)_2P$], 1.51 (br. m, 8 H, PCH_2CH_3), 1.19 (t, 9 H, BCH_2CH_3, $^3J_{HH}$ = 7.3 Hz), 1.11 (m, 12 H, PCH_2CH_3), 0.87 (m, 12 H, PCH_2CH_3), 0.55 (q, 6 H, BCH_2CH_3, $^3J_{HH}$ = 7.3 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 121.5 MHz): δ = 52.3 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.8 MHz): δ = 166.0 (s, $OCHO$), 21.6 [m, $P(CH_2)_2P$], 21.4 (m, PCH_2CH_3), 19.5(br., BCH_2CH_3), 18.0 (m, PCH_2CH_3), 12.6 (s, BCH_2CH_3), 9.3 (s, PCH_2CH_3), 7.9 (s, PCH_2CH_3) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 293 K, 96.2 MHz): δ = 0.3 (br., 1 B, $NBEt_3$) ppm. IR (ATR): $\tilde{\nu}$ = 1611 [ν_{asym}(COO)], 1320 [ν_{sym}(COO)] cm^{-1}. $C_{27}H_{64}BMoNP_4O_2$ (665.44): calcd. C 48.73, H 9.69, N 2.11; found C 48.91, H 9.75, N 2.15.

Preparation of *trans*-Mo[$^1\eta$-OCH(PhCl)$_2$](NBEt$_3$)(depe)$_2$ (10): 15.4 mg (0.061 mmol, 1.1 equiv.) of 4,4′-dichlorobenzophenone was added to a [D$_8$]toluene solution (0.7 mL) of Mo(H)(NBEt$_3$)(depe)$_2$ (34 mg, 0.055 mmol). After 1 d at 60 °C, the solvent was removed under vacuum to afford a light orange powder. The precipitate was washed with pentane and then the product was extracted with diethyl ether. Crystallization from diethyl ether at –30 °C gave yellow single crystals. Yield of **10**: 37.9 mg, 0.043 mmol, 80%. ^{1}H NMR ([D$_8$]toluene, 293 K, 500.2 MHz): δ = 6.92 (d, 4 H, Ph, $^3J_{HH}$ = 8.4 Hz), 6.78 (d, 4 H, Ph, $^3J_{HH}$ = 8.4 Hz), 4.68 (s, CHO), 2.12–2.00 [br., 8 H, $P(CH_2)_2P$], 1.48 (br., 8 H, PCH_2CH_3), 1.29 (br., 8 H, PCH_2CH_3), 1.06 (m, 12 H, PCH_2CH_3), 1.04 [t, 9 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.7 Hz], 0.79 (m, 12 H, PCH_2CH_3), 0.35 [q, 6 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.4 Hz] ppm. $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 293 K, 121.5 MHz): δ = 48.15 (s, 4 P) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 293 K, 125,8 MHz): δ = 150.8 (s, *i*-Ph), 131.5 (s, *p*-Ph), 129.0 (t, Ph), 128.0 (t, Ph), 83.1 (s, OCH), 21.8–21.6 [m, $P(CH_2)_2P$ and PCH_2CH_3], 20.9–20.1 [br., $B(CH_2CH_3)_3$], 19.9 (PCH_2CH_3), 12.9 [s, $B(CH_2CH_3)_3$], 9.1 (s, PCH_2CH_3), 8.4 (s, PCH_2CH_3) ppm. ^{11}B NMR ([D$_8$]toluene, 293 K, 96.2 MHz): δ = 3.5 [br., $B(CH_2CH_3)_3$] ppm. $C_{39}H_{72}BCl_2MoNOP_4$ (872.54): calcd. C 53.68, H 8.32, N 1.61; found C 53.67, H 8.36, N 1,63.

Preparation of *trans*-Mo[$^1\eta$-OCH(Me)Ph](NBEt$_3$)(depe)$_2$ (11): Complex **8** (36.8 mg, 0.059 mmol) was dissolved in 0.5 mL of C_6D_6 in a Young NMR tube. Then acetophenone (6.9 µL, 0.059 mmol) was added by a micro-syringe. After 3 d of standing at room temperature, the solution was concentrated under vacuum and the solid was dissolved in diethyl ether, the solution filtered through Celite and put in a refrigerator at –30 °C where yellow crystals were obtained. Yield of **11**: 40.5 mg, 0.054 mmol, 92%. ^{1}H NMR (C_6D_6, 293 K, 300.1 MHz): δ = 7.11–6.97 (m, 5 H, Ph), 4.11 [q, 1 H, OCH(Me)Ph, $^3J_{HH}$ = 6.3 Hz], 2.20 (br. m, 8 H, PCH_2Me), 1.75 [br. m, 4 H, $P(CH_2)_2P$], 1.60–1.54 (br. m, 8 H, PCH_2Me), 1.38 [br. m, 4 H, $P(CH_2)_2P$], 1.25 (t, 9 H, BCH_2CH_3, $^3J_{HH}$ = 7.5 Hz), 1.18 (m, 12 H, PCH_2CH_3), 0.96 (d, 3 H, $OCHCH_3Ph$, $^3J_{HH}$ = 6 Hz), 0.92 (m, 12 H, PCH_2CH_3), 0.52 (q, 6 H, BCH_2Me, $^3J_{HH}$ = 7.5 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 121.5 MHz): δ = 48.1 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.8 MHz): δ = 128.0–126.7 (m, Ph), 75.1 (s, $OCHMePh$), 30.3 [s, $OCH(CH_3)Ph$], 21.8 [m, $P(CH_2)_2P$], 21.4 (m, PCH_2CH_3), 19.9 (br., BCH_2Me), 17.3–17.6 (m, PCH_2Me), 13.1 (s, BCH_2CH_3), 9.5 (s, PCH_2CH_3), 8.2 (s, PCH_2CH_3) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 293 K, 96.2 MHz): δ = –2.5 (s, 1 B, $NBEt_3$) ppm. $C_{34}H_{72}BMoNP_4O$ (741.58): calcd. C 55.07, H 9.79, N 1.89; found C 55.25, H 10.01, N 1.90.

Preparation of *trans*-Mo(NBEt$_3$)[(µ-OCH)Fe(CO)$_4$](depe)$_2$ (12): 6.74 µL (0.05 mmol) of pentacarbonyliron was added to a [D$_8$]toluene solution (0.7 mL) of hydride **8** (13 mg, 0.05 mmol). After 30 min at room temperature, the solution was filtered through Celite and the solvent was removed under vacuum to afford a light orange powder. Then the product was extracted with toluene. Crystallization from toluene at –30 °C gave yellow single crystals. Yield of **12**: 35.7 mg, 0.044 mmol, 88%. ^{1}H NMR ([D$_8$]toluene, 293 K, 500.2 MHz): δ = 13.78 (s, CHO), 1.90–1.66 [br., 10 H, $P(CH_2)_2P$ and PCH_2CH_3], 1.65–1.44 (br., 8 H, PCH_2CH_3), 1.47–1.34 [br., 10 H, $P(CH_2)_2P$ and PCH_2CH_3], 1.02 (m, 12 H, PCH_2CH_3), 0.98 [t, 9 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.8 Hz], 0.91 (m, 12 H, PCH_2CH_3), 0.34 [q, 6 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.7 Hz] ppm. $^{31}P\{^1H\}$ NMR ([D_8]toluene, 293 K, 81.0 MHz): δ = 52.2 (s) ppm. $^{13}C\{^1H\}$ NMR ([D_8]toluene, 293 K, 125 MHz): δ = 293.2 (br., OCH), 219.2 [s, $Fe(CO)_4$], 21.9 [br., $P(CH_2)_2P$ and PCH_2CH_3], 19.1 [br., $B(CH_2CH_3)_3$], 18.4 (m, PCH_2CH_3), 12.4 [s, $B(CH_2CH_3)_3$], 8.7 (s, PCH_2CH_3), 7.7 (s, PCH_2CH_3) ppm. ^{11}B NMR ([D_8]toluene, 293 K, 96.2 MHz): δ = 1.9 [br., $B(CH_2CH_3)_3$] ppm. IR (ATR): $\tilde{\nu}$ = 2020, 1966, 1870 {$\nu[Fe(CO)_4]$} cm^{-1}. $C_{31}H_{64}BFeMoNO_5P_4$ (817.33): calcd. C 45.55, H 7.89, N 1.71; found C 45.19, H 8.04, N 1.91.

Preparation of *trans*-$Mo(NBEt_3)[(\mu\text{-}OCH)Re_2(CO)_9](depe)_2$ (13): 1.06 equiv. (50.9 mg, 0.078 mmol) of $Re_2(CO)_{10}$ was added to a [D_8]-toluene solution (0.7 mL) of complex **8** (45.6 mg, 0.073 mmol). The reaction proceeded smoothly at room temperature and seemed to reach equilibrium after 2 d. The solvent was removed under vacuum and the excess of hydride was extracted with pentane. Crystallization from toluene at –30 °C gave orange single crystals. Yield of **13**: 82.5 mg, 0.065 mmol, 88%. ^1H NMR ([D_8]toluene, 293 K, 300.1 MHz): δ = 14.91 (s, CHO), 1.92–1.82 [br., 10 H, $P(CH_2)_2P$ and PCH_2CH_3], 1.65–1.44 (br., 8 H, PCH_2CH_3), 1.47–1.38 [br., 10 H, $P(CH_2)_2P$ and PCH_2CH_3], 1.02 (m, 12 H, PCH_2CH_3), 0.95 [t, 9 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.8 Hz], 0.88 (m, 12 H, PCH_2CH_3), 0.55 [q, 6 H, $B(CH_2CH_3)_3$, $^3J_{HH}$ = 7.5 Hz] ppm. $^{31}P\{^1H\}$NMR ([D_8]toluene, 293 K, 121.5 MHz): δ = 54.4 (s) ppm. $^{13}C\{^1H\}$ NMR ([D_8]toluene, 293 K, 75.5 MHz): δ = 289.5 (br., OCH), 196.2 [s, $Re(CO)_9$], 21.8 [m, $P(CH_2)_2P$ and PCH_2CH_3], 19.3 [br., $B(CH_2CH_3)_3$], 18.3 (m, PCH_2CH_3), 11.4 [s, $B(CH_2CH_3)_3$], 8.9 (s, PCH_2CH_3), 7.6 (s, PCH_2CH_3) ppm. ^{11}B NMR ([D_8]toluene, 293 K, 96.2 MHz): δ = 2.0 [br., $B(CH_2CH_3)_3$] ppm. IR (ATR): $\tilde{\nu}$ = 2094, 2070, 2025, 2007, 1969, 1935, 1902 {$\nu[Re_2(CO)_9]$} cm^{-1}. $C_{36}H_{64}BMoNO_{10}P_4Re_2$ (1273.95): calcd. C 33.94, H 5.06, N 1.10; found C 34.23, H 5.22, N 1.12.

Preparation of *trans*-$Mo(OPh)(NBEt_3)(depe)_2$ (14): Complex **8** (34 mg, 0.055 mmol) was dissolved in 0.4 mL of [D_8]toluene in a Young NMR tube and phenol (6 mg, 0.064 mmol) was added. The reaction occurred instantaneously. The solvent was removed under vacuum and the residue was extracted into diethyl ether and the solution filtered through Celite. The product **14** crystallized from diethyl ether at –30 °C to afford yellow crystals. Yield of **14**: 24 mg, 0.034 mmol, 61%. ^1H NMR (C_6D_6, 293 K, 300.1 MHz): δ = 7.08 (d, 2 H, *m*-Ph, $^1J_{HH}$ = 7.5 Hz), 6.54 (t, 1 H, *p*-Ph, $^1J_{HH}$ = 7.8 Hz), 5.91 (d, 2 H, *o*-Ph, $^1J_{HH}$ = 8.1 Hz), 2.23 (br. m, 4 H, PCH_2CH_3), 2.14 (br. m, 4 H, PCH_2CH_3), 1.70 (br. m, 4 H, PCH_2CH_3), 1.63 [br. m, 8 H, $P(CH_2)_2P$], 1.38 (br. m, 4 H, PCH_2CH_3), 1.22 (t, 9 H, BCH_2CH_3, $^3J_{HH}$ = 7.5 Hz), 1.18 (m, 12 H, PCH_2CH_3), 0.83 (m, 12 H, PCH_2CH_3), 0.55 (q, 6 H, BCH_2CH_3, $^3J_{HH}$ = 7.5 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K, 121.5 MHz): δ = 52.4 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K, 125.8 MHz): δ = 129.0 (s, *m*-Ph), 119.5 (s, *o*-Ph), 114.0 (s, *p*-Ph), 21.8 [m, $P(CH_2)_2P$], 21.5 (m, PCH_2CH_3), 19.5 (br., BCH_2CH_3), 17.3 (m, PCH_2CH_3), 12.9 (s, BCH_2CH_3), 9.6 (s, PCH_2CH_3), 7.8 (s, PCH_2CH_3) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6, 293 K, 96.2 MHz): δ = –0.9 (br., 1 B, $NBEt_3$) ppm. IR (ATR, 22 °C): $\tilde{\nu}$ = 1309 [ν(OPh)] cm^{-1}. $C_{32}H_{68}BMoNP_4O$ (713.53): calcd. C 53.86, H 9.61, N 1.96; found C 53.71, H 9.33, N 1.84.

Attempt of Stoichiometric "Ionic Hydrogenation" of Acetone by 8 in the Presence of Phenol: Compound **8** (6.3 mg, 0.01 mmol) was dissolved in 0.4 mL of [D_8]THF in a Young NMR tube. Then 0.73 µL of acetone (0.58 mg, 0.01 mmol) and PhOH (1 mg, 0.01 mmol) were added. Formation of complex **14** was detected by NMR spectroscopy. A product of hydrogenation could not be observed.

Hydrogenation of Cyclohexene: To a [D_8]toluene solution (0.7 mL) of $Mo(H)(NBEt_3)(depe)_2$ (**8**) (3.8 mg, 0.006 mmol) was added 66 µL (0.65 mmol) of cyclohexene in a Young NMR tube. The reaction mixture was degassed in 3 freeze-pump-thaw cycles. H_2 (1400 mbar) was applied at 77 K. The catalytic reaction was carried out at 110 °C. After 24 h, cyclohexane (8%) could be detected spectroscopically. In the ^{31}P NMR spectrum characteristic signals of the free phosphane ligand were observed. After an additional period of 31 h, the amount of cyclohexane was 25% and it had hardly changed after 45 h. Another flush of H_2 (1739 mbar) was then introduced at 77 K to the solution mixture. After 9 d at 110 °C, the amount of cyclohexane had reached 94%. Cyclohexane: ^1H NMR ([D_8]toluene, 300 MHz, 20 °C): δ = 1.34 (s, 6 H). GC-MS: t_r = 1.63 min; m/z = 83 [M^+].

X-ray Crystal Structure Analyses: Crystallographic data for compounds **4**, **6**, **8**–**10** and **12**–**14** are collected in Tables 1 and 2. All crystals were embedded in polybutene oil within a glove box, mounted on glass fibers and fixed by a cold N_2 stream of an Oxford Cryogenic System at the diffractometer. Measurement temperatures of 153(2) K for compound **6**, 173(2) K for compound **4** and 183(2) K for the remaining compounds were used. An imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used for the exposure of 222, 176, 200, 182, 200, 236, 300 and 187 images at constant times of 3.5, 3.0, 1.6, 8.0, 4.0, 6.0, 4.0 and 3.0 min per image.[61] The crystal-to-image distances were set to 50 mm for **6**, **8**, **9**, **10**, **12** and **14**, to 64 mm for **13** and to 70 mm for **4**; φ-rotation (for **6** and **8**) and φ-oscillation modes (for **4**, **9**, **10**, **12**, **13** and **14**) were necessary for the increments of 1.7 and 1.1° or of 0.9, 1.0, 1.0, 1.1, 0.7 and 1.0° per exposure in each case. The intensities were integrated by using a dynamic peak profile analysis, and an estimated mosaic spread (EMS) check was performed to prevent overlapping intensities. For the cell parameter refinements, 7998 (**4**, **12** and **14**), 8000 (**8** and **9**) and 8001 reflections[61] (**6**, **10** and **13**) were selected out of the whole limiting spheres with intensities $I > 6\sigma(I)$. A total of 59134, 12588, 43658, 37490, 53007, 33565, 43402 and 23754 reflections were collected, of which 16225, 3869, 9585, 10353, 12539, 11856, 10343 and 11186 were unique after performing absorption correction and data reduction (R_{int} = 16.02, 5.62, 8.57, 11.06, 8.70, 7.43, 4.99 and 8.77%). A total of 12, 10, 10, 11, 12, 12, 10 and 15 indexed crystal faces were used for the numerical absorption corrections.[62] The structures were solved with the merged unique data set after checking for correct space groups. The Patterson method was used to solve the crystal structures by applying the software options of the program SHELXS-97.[63] The structure refinements were performed with the program SHELXL-97.[63] The programs PLATON[64] and PLUTON[65] were used to check the results of the X-ray analyses. The crystal structure of compound **4** showed a superstructure with three independent complexes in the asymmetric unit of the monoclinic cell (space group $P2_1/c$). A complete check with PLATON[64] did not suggest a higher symmetry system or space group. Compound **6** crystallized in the centrosymmetric triclinic space group $P\bar{1}$. The Mo atoms of the structure lie on centers of inversion; thus, only half of the molecule had to be refined. As a consequence, a disorder between the NBH_3 and Cl ligands was observed. The hydrogen atoms of the BH_3 group were located by difference electron density calculations. The geometry of the BH_3 group has been corrected by using B–H and H···H distance restraints and the coordinates of the H atoms were finally fixed dur-

Table 1. Crystallographic details of **4**, **6**, **8** and **9**.

	4	**6**	**8**	**9**
Empirical formula	$C_{20}H_{48}ClMoNP_4$	$C_{20}H_{51}BClMoNP_4$	$C_{26}H_{64}BMoNP_4$	$C_{27}H_{64}BMoNO_2P_4$
Color	orange	yellow	yellow	yellow
M_r [g mol^{-1}]	557.86	571.70	621.41	665.42
Crystal size [mm]	0.21 × 0.20 × 0.13	0.17 × 0.15 × 0.07	0.44 × 0.34 × 0.08	0.27 × 0.13 × 0.10
T [K]	173(2)	153(2)	183(2)	183(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	23.4140(13)	8.2157(8)	10.4337(8)	9.4820(11)
b [Å]	13.7435(7)	8.9506(9)	18.3864(10)	20.5582(19)
c [Å]	26.0626(13)	10.1080(10)	17.6487(15)	17.946(2)
α [°]	90	94.918(12)	90	90
β [°]	90.727(6)	98.569(12)	96.230(10)	97.262(13)
γ [°]	90	103.428(11)	90	90
V [Å^3]	8386.0(8)	709.29(12)	3365.7(4)	3470.2(6)
Z	12	1	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.326	1.338	1.226	1.274
μ [mm^{-1}]	0.801	0.790	0.595	0.586
F(000)	3528	302	1336	1424
Transmission range	0.850–0.903	0.877–0.947	0.747–0.945	0.891–0.960
2θ range [°]	$2.15 < 2\theta < 25.91$	$2.59 < 2\theta < 30.32$	$2.63 < 2\theta < 30.45$	$2.49 < 2\theta < 30.38$
Measured reflections	59134	12588	43658	37490
Unique reflections	16225	2351	9585	10353
$I > 2\sigma(I)$ reflections	4924	2086	6777	5128
Parameters	740	131	312	330
Goodness-of-fit (for F^2)	0.500	0.992	0.842	0.742
$R_1[I > 2\sigma(I)]$, R_1(all data)[a]	0.0401, 0.1508	0.0263, 0.0311	0.0302, 0.0461	0.0453, 0.1103
$wR_2[I > 2\sigma(I)]$, wR_2(all data)[a]	0.0590, 0.0760	0.0664, 0.0675	0.0667, 0.0695	0.0907, 0.1033
$\Delta\rho_{max/min}$	0.451/–0.541	0.300/–0.656	0.596/–1.086	0.859/–1.204

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $wR_2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$.

Table 2. Crystallographic details of **10**, **12**, **13** and **14**.

	10	**12**	**13**	**14**
Empirical formula	$C_{39}H_{72}BCl_2MoNOP_4$	$C_{31}H_{64}BFeMoNO_5P_4$, $0.5C_7H_8$	$C_{36}H_{64}BMoNO_{10}P_4Re_2$	$C_{32}H_{68}BMoNOP_4$
Color	yellow	yellow	orange	yellow
M_r [g mol^{-1}]	872.51	863.38	1273.91	713.50
Crystal size [mm]	0.23 × 0.21 × 0.07	0.15 × 0.13 × 0.10	0.17 × 0.15 × 0.08	0.36 × 0.31 × 0.11
T [K]	183(2)	183(2)	183(2)	183(2)
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	13.6170(14)	10.9338(15)	11.8594(8)	10.2952(11)
b [Å]	19.5423(17)	11.2735(17)	12.1646(7)	19.6339(19)
c [Å]	16.8397(14)	19.924(3)	32.705(3)	18.6052(17)
α [°]	90	96.882(17)	90	90
β [°]	91.283(11)	94.450(17)	98.271(9)	91.236(12)
γ [°]	90	116.307(15)	90	90
V [Å^3]	4480.0(7)	2162.0(5)	4669.0(5)	3759.9(6)
Z	4	2	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.294	1.326	1.812	1.260
μ [mm^{-1}]	0.585	0.810	5.624	0.544
F(000)	1848	910	2496	1528
Transmission range	0.883–0.962	0.886–0.936	0.662–0.422	0.848–0.936
2θ range [°]	$2.82 < 2\theta < 30.39$	$2.73 < 2\theta < 30.37$	$2.09 < 2\theta < 27.21$	$2.47 < 2\theta < 30.42$
Measured reflections	53007	33565	43402	41417
Unique reflections	12539	11856	10343	11186
$I > 2\sigma(I)$ reflections	5568	6234	8139	6042
Parameters	451	423	507	367
Goodness-of-fit (for F^2)	0.617	0.682	0.879	0.753
$R_1[I > 2\sigma(I)]$, R_1(all data)[a]	0.0344, 0.0996	0.0356, 0.0897	0.0225, 0.0314	0.0395, 0.0857
$wR_2[I > 2\sigma(I)]$, wR_2(all data)[a]	0.0562, 0.0649	0.0558, 0.0631	0.0530, 0.0541	0.0840, 0.0917
$\Delta\rho_{max/min}$	0.588/–0.992	0.718/–0.921	0.708/–0.849	1.083/–0.912

[a] $R_1 = \Sigma(F_o - F_c)/_\Sigma F_o$; $wR_2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$.

ing the last refinement. For compound **8** the position of the hydride atom H27 was also located by difference electron density calculations but all its parameters were freely refined while the other positions of hydrogen atoms were calculated after each refinement cycle. Compound **9** crystallized in the centrosymmetric monoclinic space group $P2_1/n$. Large anisotropic displacement parameters were observed for two ethyl groups on the boron atom and for one ethyl group on the phosphorus atom P3. The disorder refinement for these ethyl groups done with distance restraints improved significantly the result, the atomic splitting was kept and the corresponding carbon atoms were refined isotropically. For compound **10** one ethyl group on the phosphorus atom P2 was treated for disorder and isotropically refined. Compound **12** crystallized in the triclinic space group $P\bar{1}$. One toluene solvent molecule cocrystallized with the structure and is located near a center of inversion leading to a disorder. Many FREE instructions were necessary to calculate the positions of H atoms of the disordered toluene, and the corresponding carbon atoms were refined isotropically. One ethyl group on the boron atom B1 in compound **14** was found to be positionally disordered. All structures in this paper crystallize in centrosymmetric triclinic or monoclinic space groups, except the structure of **2** given in the Supporting Information. CCDC-280778 to -280788 and CCDC-249319 (for **1**–**4**, **6**, **8**–**10** and **12**–**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ORTEP representations and crystallographic details of compounds **1**, **2** and **3**.

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